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X-Ray and Mössbauer Study of Magnetic Black Sand from Mayotte Island

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Abstract

Natural magnetic black sands are known from several sites often located in areas of volcanic origin. Their elemental and mineral composition provides information on the geology of their territory and depends on several factors occurred during their formation. A sample of black sand was collected on the seashore of the island of Mayotte in the Indian Ocean and its magnetic part was investigated by means of energy dispersive X-ray spectroscopy (EDS), powder X-ray diffraction (XRD), and Mössbauer spectroscopy at room temperature. The mineral composition is dominantly magnetite, in good agreement with samples collected in other sites of volcanic origin. Contrary to pure magnetite, a relevant fraction of Ti was detected by EDS. The 16% Ti and 1% Mn content increase the magnetite lattice parameter to 8.4312 (25) Å. The broadening of XRD lines pointed towards a significant degree of disorder. This was confirmed by Mössbauer spectroscopy and is attributed to the presence of Ti replacing Fe in the magnetite lattice. The presence of Ti modifies the local magnetic field on the Fe sites, leading to a broader and more complex Mössbauer transmission spectrum with respect to the one of pure magnetite. To study the effect of temperature, samples were heated for 12 hours to 600˚C and 800˚C in argon and to 1000˚C in air. Annealing in argon did not improve the crystallinity while annealing in air caused a complete decomposition of magnetite into hematite and pseudobrookite.

Keywords

Magnetic Black Sand, Iron Minerals, Energy Dispersive X-Ray Spectroscopy, X-Ray Diffraction, Mössbauer Spectroscopy

1. Introduction

The natural occurrence of strongly magnetic black sands is known from several sites, e.g. in Italy [1], the Black Sea [2], or Costa Rica [3]. Often these sands are of volcanic origin. After erosion of the primary rock, the heavy sands accumulate in alluvial deposits. Due to their high iron oxide content, some deposits attracted interest for mining as iron ore.

The chemical structure of natural samples depends on several factors and conditions occurred during their formation. In particular, the presence of elements different from iron, pressure and time of solidification determine changes in the structure that can be put in evidence and quantitatively studied by means of the experimental methods used in this work.

Due to their high iron content, magnetic black sands are radiopaque and, if present in sufficient quantity, can be detected within biological tissues using radiology based imaging techniques. If ingested or inhaled, magnetic black sands may lead to artifacts in medical imaging techniques (radiography, computed tomography (CT)).

This work originated from a case in forensic medicine. CT imaging revealed the presence of a highly radiopaque object in the trachea of a newborn corpse found on a beach of the isle of Mayotte [4]. The autopsy was performed some days later and showed only the presence of compact black sand in the esophagus and in the trachea. A characterization of this natural material was then performed and allowed demonstrating that compact radiopaque magnetite black sand faked the shape of a metallic weapon. The results of this characterization were found to be interesting beyond this study since the composition of magnetic black sand from Mayotte differs from the one of already published natural samples.

Along the lines of this case in forensic medicine, a sample of magnetic black sand from Mayotte Island was analyzed with the same methodology used in a previous study of black sand from the Mediterranean Sea near Rome [1]. In particular, the mineral and chemical composition were analyzed by energy dispersive X-ray spectroscopy (EDS) [5], powder X-ray diffraction (XRD) [5], and Mössbauer spectroscopy [6]. Radioactivity was assessed via hyper-pure germanium (HPGe) gamma spectroscopy [7].

2. Materials and Methods

A sample of natural black sand was collected from a beach situated on the north coast of Mayotte, a French over-sea department situated in the northern Mozambique Channel off the coast of southeast Africa. The sample was separated into a magnetic and a non-magnetic component by means of a strong permanent magnet. The magnetic fraction accounts for about 95% of the total mass, as reported in **Table 1**. Only the magnetic fraction was further characterized.

From the separated magnetic component three further samples were prepared. They were heated in a porcelain crucible inside a tubular furnace for 12 hours to 600˚C and 800˚C under argon and to 1000˚C in air.

The elemental composition of the magnetic fraction was analyzed by energy disper-

sive X-ray spectroscopy using a Noran SIX NSS200 (Thermo Electron Corporation, Madison, WI, USA) detector attached to a Hitachi scanning electron microscope S-3000 N (Hitachi High-Technologies Europe GmbH, Krefeld, Germany).

Powder X-ray diffraction patterns were measured on a Stoe StadiP powder diffractometer (STOE & Cie. GmbH, Darmstadt, Germany) in reflection geometry (Bragg-Brentano) at room temperature. Cu $K_{\alpha 1}$ radiation (λ = 1.540598 Å) was used from a focusing α-quartz (101) monochromator. Diffraction patterns were measured from 15˚ to 100˚ 2-Theta with a resolution of 0.01˚ using a position sensitive detector. Due to the vast iron content, the samples show a strong absorption of Cu K_{α} radiation and concomitant an intense X-ray fluorescence from Fe. The high background due to the X-ray fluorescence was subtracted from the data.

A Mössbauer spectrometer (Fast Com Tec MA-250) equipped with a 5 mCi ^{57}Co source in a Rh matrix was employed. A proportional tube filled with 97% Kr and 3% CO_2 at 1 atm pressure with a thin Be side window (LND 45431) was used to detect the 14.4 keV characteristic Mössbauer line.

3. Experimental Results

Three mm-sized black shiny grains belonging to the magnetic component were selected and analyzed by EDS. They turned out to be exactly identical in their composition and are therefore taken as representative for the sample. The elemental composition in atom% with respect to the metal atoms is reported in Table 2. The oxygen content is not quantitatively accessible by this method. The sample contains mainly iron with a significant amount of titanium and a small amount of manganese, all in the form of oxide compounds.

Powder X-ray diffraction patterns of the magnetic component and of samples heated under argon to 600˚C and 800˚C are shown in Figure 1. The diffraction pattern of the magnetic fraction, the black trace in Figure 1, corresponds to a cubic magnetite phase

Table 1. Results of the magnetic separation of the sample. The uncertainties are reported in parenthesis.

Component	Mass (g)	Fraction (%)
Magnetic	1.9362	95 (1)
Non-magnetic	0.0979	5 (1)
Total	2.0341	100

Table 2. EDS analysis of the magnetic fraction. The uncertainties are reported in parenthesis.

Element	Atom (%)
Fe	82.8 (4)
Ti	16.2 (3)
Mn	1.0 (3)

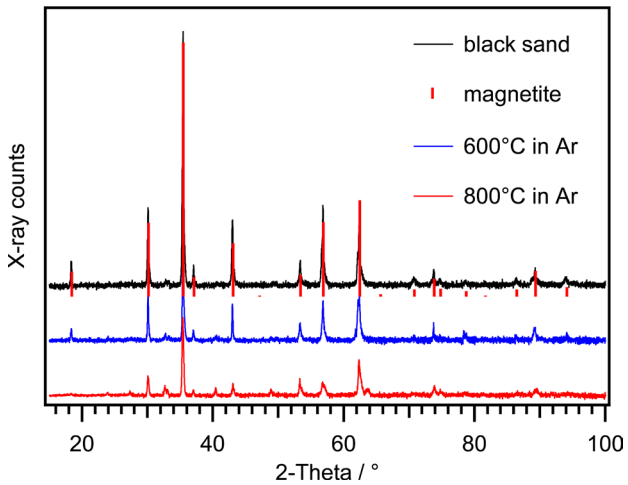

Figure 1. Powder X-ray diffraction patterns of the magnetic fraction (black line) and under argon gas thermally processed samples at 600˚C (blue line) and 800˚C (red line). The Bragg peak positions and intensities of magnetite are shown as reference (red ticks). Patterns were measured with Cu $K_{\alpha 1}$ radiation (λ = 1.540598 Å) at room temperature.

with space group Fd-3m. A calculated pattern is shown as red ticks below the black trace. The positions and the intensities of the Bragg peaks agree very well between measured and calculated patterns. Only a minor peak around 33˚ 2-Theta does not belong to the magnetite phase.

The cubic lattice parameter was refined with the STOE WinXPow diffractometer software as a = 8.4312 (25) Å. It is slightly bigger than for pure magnetite Fe_3O_4 for which a typical parameter value of a = 8.3930 (6) Å was found in literature [8].

The increase of the lattice parameter is due to the significant Ti content of the sample. Ti^{4+} replaces Fe^{3+} on the tetrahedral site of the spinel lattice. The ionic radii are 0.42 Å for Ti^{4+} and 0.49 Å for Fe^{3+} for four-fold coordination (CN = 4) [9]. Due to the different valence of Ti^{4+} vs. Fe^{3+} charge compensation is required. It can be achieved in various ways, e.g., by replacing an octahedral Fe^{3+} by Fe^{2+}. The respective ionic radii for CN = 6 are 0.645 Å for high spin (HS) Fe^{3+} and 0.78 Å for HS Fe^{2+}. Accordingly, the replacement of Fe^{3+} (CN = 4) and Fe^{3+} (HS, CN = 6) by Ti^{4+} and Fe^{2+} (HS, CN = 6) results in a lattice expansion. Another realistic mechanism for the charge compensation of the Ti^{4+}/Fe^{3+} substitution is the creation of cation defects.

The diffraction pattern shows rather broad peaks, which indicate a significant degree of disorder in the magnetite phase. Above about 50˚ 2-Theta, the peaks show indications for splitting which may be due to lattice distortions towards lower symmetry.

It was attempted to improve the crystallinity of the material by heating the sample in argon to 600˚C and 800˚C. The corresponding diffraction patterns are shown in **Figure 1** as blue and red traces, respectively. The crystallinity was not improved by heating. Rather in contrast, a partial decomposition is observed. Additional weak Bragg peaks occur, especially for the sample heated to 800˚C. They are due to the formation of hematite Fe_2O_3 (space group R-3c) [9] and pseudobrookite Fe_2TiO_5 (space group Ccmm) [10] [11]. The pattern of the sample heated to 1000˚C in air is reported in **Figure 2**. It

shows a complete decomposition of the magnetite phase into hematite and pseudo-brookite. The decomposition is driven by the oxidation of Fe(II) to Fe(III) in air and the separation of Ti from the magnetite into the Fe_2TiO_5 phase.

Mössbauer spectroscopy was performed at room temperature on the natural sample as well as on the samples obtained after annealing at 600˚C and 800˚C in Ar, and at 1000˚C in air. More than 10^6 events per channel were collected for all spectra in order to reduce the statistical uncertainty at a level of less then 10^{-3} on each channel. The spectra were compared to the one obtained by analyzing the magnetic part of a black sand sample collected from the seashore of Ladispoli in Italy [1], see **Figure 3**.

The spectrum in **Figure 3** can be interpreted as almost pure magnetite with iron in both tetrahedral and octahedral sites and can be fitted by two sextets, as reported in

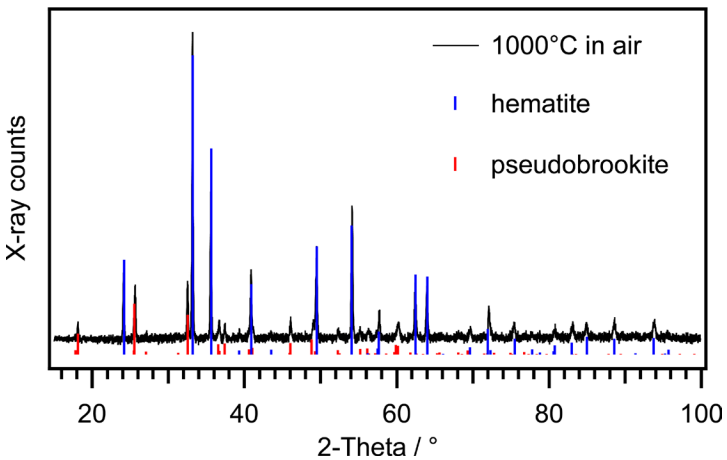

Figure 2. Powder X-ray diffraction pattern of a sample heated in air to 1000˚C. The pattern changed completely from magnetite to hematite and pseudobrookite. The pattern was measured with Cu $K_{\alpha 1}$ radiation (λ = 1.540598 Å) at room temperature.

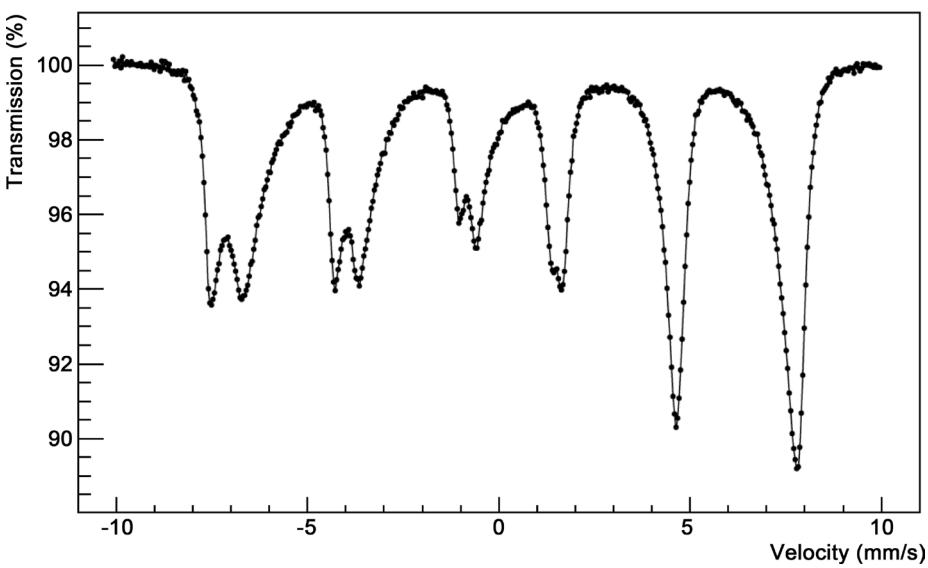

Figure 3. Mössbauer transmission spectrum of magnetic separated black sand from Ladispoli (Italy) corresponding to almost pure magnetite with iron in both tetrahedral and octahedral sites.

Table 3. For the isomeric shift (IS) the data are referred to α-Fe taken as zero. These results are in agreement with literature [1], where only a non-magnetically separated sample was analyzed by Mössbauer spectroscopy. The transmission spectra obtained with the sample from Mayotte island are reported in Figure 4.

The natural sample presents a complex spectrum with enhancements that correspond to the characteristic peaks of magnetite with iron in both tetrahedral and octahedral sites, as reported in literature [1] and in agreement with Figure 3 and Table 3. Contrary to the black sand from Ladispoli, the sample from Mayotte indicates a significant disorder in the magnetite phase in agreement with powder X-ray diffraction

Table 3. Mössbauer parameters of the fit performed on the transmission spectrum obtained with the magnetic separated sample of sand from Ladispoli (Italy).

χ^2/ndf	Function	HF	QS	IS	Area	AR	AS
		[T]	[mm/s]	[mm/s]	[%mm/s]	[%]	
2.0	Sextet 1	47.59	−0.02	0.28	16.0	30.4	Mag.A
	Sextet 1	44.14	−0.05	0.60	36.5	69.6	Mag.B

HF: hyperfine splitting magnetic field, QS: quadrupole splitting, IS: isomeric shift, AR: area ratio, AS: assignment, Mag. A: magnetite with iron on tetrahedral sites, Mag. B: magnetite with iron on octahedral sites.

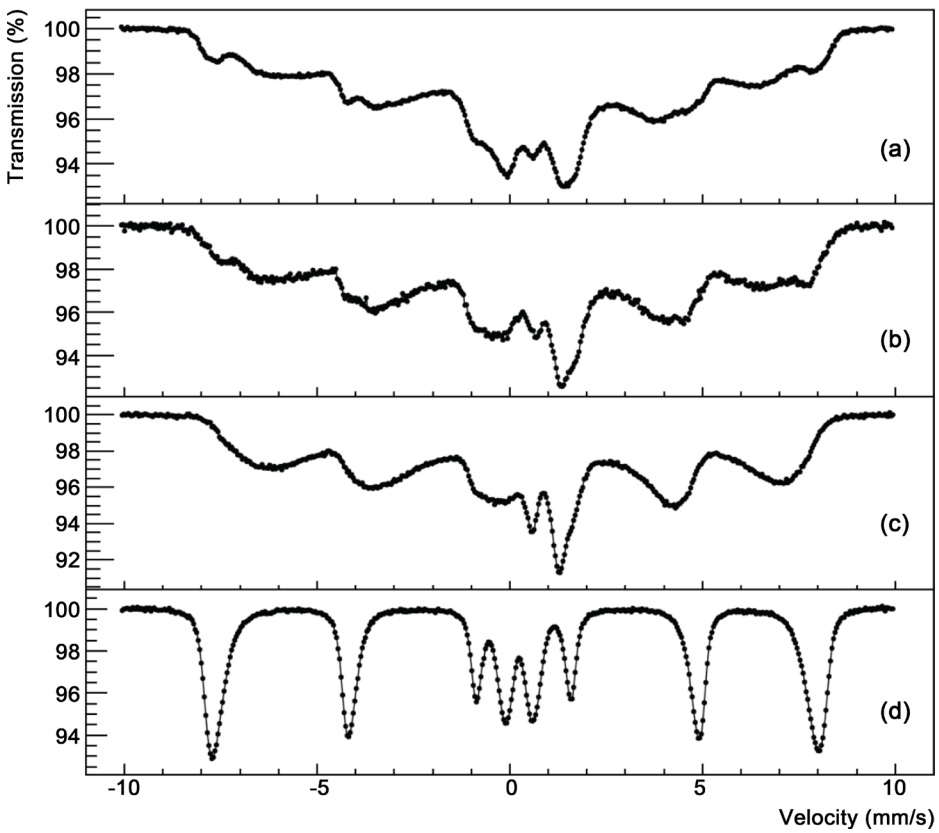

Figure 4. Mössbauer transmission spectra of magnetic separated black sand from Mayotte island: natural sample (a); after 12 hour annealing in Ar at 600˚C (b) and at 800˚C (c); after 12 hour annealing at 1000˚C (d) in air.

Table 4. Mössbauer parameters of the fit performed on the transmission spectrum obtained with the magnetic separated sample of sand from Mayotte heated at 1000˚C in air.

χ^2/ndf	Function	HF	QS	IS	Area	AR	AS
		[T]	[mm/s]	[mm/s]	[%mm/s]	[%]	
5.2	Sextet	48.60	−0.21	0.36	22.8	78.6	Hematite
	Doublet		0.61	0.35	6.24	21.4	Pseudobrookite

HF: hyperfine splitting magnetic field, QS: quadrupole splitting, IS: isomeric shift, AR: area ratio, AS: assignment.

results. This disorder affects the magnetic field on the iron sites, determining strong broadening effects in the spectrum. Annealing at 600˚C and 800˚C in Ar slightly improve the sharpness of the enhancements. Although the position of the enhancements correspond to magnetite, a fit of the transmission spectrum is not feasible.

As observed with powder X-ray diffraction, the sample heated to 1000˚C in air is completely transformed into hematite and pseudobrookite without any magnetite left over. The corresponding Mössbauer transmission spectrum (**Figure 4(d)**) also changes completely and can be fitted with one sextet and one doublet, compatible with hematite and pseudobrookite values reported in literature [12]. The results of the fit are reported in **Table 4**.

Traces of radioactive elements were searched for on a sample of non-magnetically separated sand by HPGe gamma spectroscopy. Naturally occurring radionuclides of terrestrial origin coming from the ^{226}Ra (115 ± 13 Bq/kg) and ^{232}Th (7 ± 5 Bq/kg) decay chains were found to be compatible with average natural radioactivity reported in literature [13].

4. Conclusion

A sample of magnetic black sand from the island of Mayotte was studied by means of EDS, XRD, and Mössbauer spectroscopy. Magnetite was found as main component, in good agreement with similar samples collected in other sites of volcanic origin. Contrary to pure magnetite, a relevant fraction of Ti was measured by EDS. Ti increases the lattice parameter of the magnetite phase. Furthermore, a significant degree of disorder in the magnetite phase was found by XRD. This was confirmed by Mössbauer spectroscopy, which showed a much broader transmission spectrum with respect to the typical magnetite pattern composed by two sextets. These effects are mostly due to Ti replacing Fe in the crystal lattice. In particular, the presence of Ti modifies the local magnetic field on the Fe sites, leading to the broader Mössbauer transmission spectrum. Samples were annealed in argon and air to study the effect of temperature on the structure. Annealing in argon did not improve the crystallinity while annealing in air caused a complete decomposition of the magnetite phase into hematite and pseudobrookite. Traces of radioactive elements were also researched and quantities compatible with naturally occurring radionuclides of terrestrial origin (Ra and Th) were found.

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